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STUDIES OF LAKE MICHIGAN BOTTOM SEDIMENTS-NUMBER SIX

TRACE ELEMENT AND ORGANIC CARBON ACCUMULATION IN THE MOST RECENT SEDIMENTS OF SOUTHERN LAKE MICHIGAN

Neil F. Shimp, John A. Schleicher, R. R. Ruch,
David B. Heck, and Harry V. Leland

ILLINOIS STATE GEOLOGICAL SURVEY

JOHN C. FRYE, Chief • Urbana 61801



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ABSTRACT

Trace elements in 21 grab samples and sections of 21 cores from southern Lake Michigan were determined. In all, 119 sediment samples were analyzed for 13 trace elements, organic carbon, and less than 2-micron clay.

Results show that bromine, chromium, copper, lead, and zinc are accumulating in the uppermost, recently deposited sediments (0 to 10 cm) of the deeper regions of southern Lake Michigan. Prominent areas of concentration occur in sediments off Grand Haven and Benton Harbor in Michigan, off Waukegan in Illinois, and in the lake center near the Illinois-Wisconsin border. Concentrations of these five trace elements generally increase as the amount of organic carbon increases.

Trace elements showing little or no accumulation in the recently deposited sediments of the southern part of the lake are beryllium, boron, cobalt, lanthanum, manganese, nickel, scandium, and vanadium.

INTRODUCTION

The research reported here is a continuation of studies on the chemical composition of southern Lake Michigan sediments begun in 1969 and is a result of cooperation between the Illinois State Geological Survey and H. V. Leland of the Civil Engineering Department of the University of Illinois. Previous reports include those by Shimp, Leland, and White (1970);

Ruch, Kennedy, and Shimp (1970); and Schleicher and Kuhn (1970). Shipboard sampling procedures and laboratory methods of analysis have been described by Gross et al. (1970), Shimp, Leland, and White (1970), and Lineback, Ayer, and Gross (1970). All determinations reported were made in the laboratories of the Illinois State Geological Survey.

Support in the form of ship time and assistance in sample collection were provided by the Great Lakes Research Division, Ann Arbor, Michigan; the Great Lakes Fishery Laboratory, U. S. Department of the Interior, Ann Arbor, Michigan; and the Federal Water Quality Administration, U. S. Department of the Interior, Chicago, Illinois. Six of the sediment cores analyzed were supplied by the Harza Engineering Company, Chicago, Illinois. Organic carbon was determined by C. W. Beeler and L. R. Camp, manganese was determined by John K. Kuhn, and the less than 2-micron clay determinations were made by W. Arthur White. All workers are members of the Survey staff.

RESULTS

Samples were taken from the locations in southern Lake Michigan shown in figure 1. The station numbers underlined (43, 44, 142, and 145) are those for which complete analyses were reported previously by Shimp, Leland, and White (1970), and the analyses are not repeated in their entirety here. However, these analyses were included in calculating statistical correlations and in mapping the abundance of trace elements in the uppermost portions of the sediments.

Brief sample descriptions and results of analyses at each sediment depth interval (depth of burial within the sediment column) for boron, beryllium, bromine, cobalt, chromium, copper, lanthanum, manganese (expressed as MnO), nickel, lead, scandium, vanadium, zinc, organic carbon, and less than 2-micron clay are given in table 1. More complete stratigraphic descriptions of the sediments in southern Lake Michigan were presented by Gross et al. (1970) and Lineback, Ayer, and Gross (1970). Trace element values given as zero in table 1 were not used in statistical evaluations of data.

The distribution of bromine, chromium, copper, lead, and zinc concentrations for different sediment depth intervals in five cores (105, 107, 113, 115, and 124) taken off Grand Haven, Michigan, are shown in figures 2 through 6. The percentage of organic carbon for each sediment depth interval is given at the right of each figure. These five trace elements and organic carbon are consistently concentrated in the uppermost part of the sediments near the water interface. In cores 105 and 107 (figs. 2 and 3), noticeable accumulation within the sediments extends to a depth of about 10 cm. This may be attributed to rapid deposition of the large load of sediment entering Lake Michigan from the nearby St. Joseph River.

The distribution of bromine, chromium, copper, lead, and zinc concentrations in Lake Michigan cores 241 and 101 are given in figures 7 and 8, and

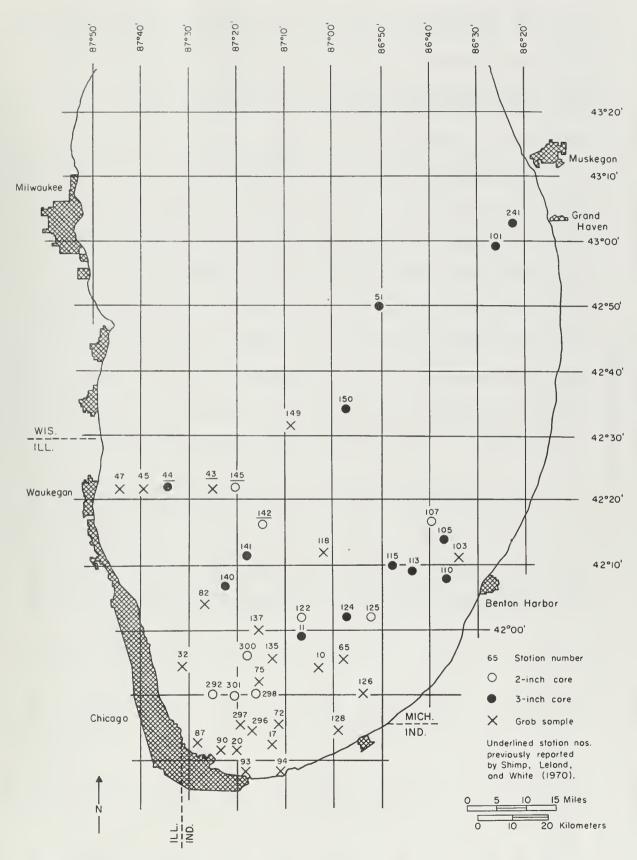


Fig. 1 - Location of the stations in southern Lake Michigan from which cores and grab samples were taken.

SAMPLE LOCATIONS AND RESULTS OF CHEMICAL ANALYSES FOR SOUTHERN LAKE MICHIGAN CORE SECTIONS AND GRAB SAMPLES TABLE 1

C(m) B Be Br Co Cr Cu La Ni Pb Sc V Zn Org. C I Jy Mn I Co Cr Cu La Ni Pb Sc V Zn Org. C I Jy Mn I Co Cr Cu La Ni Pb Sc V Zn Org. C I Jy Mn I Co Cr Cu La Ni Pb Sc V Zn C Org. C I Jy Mn I Co Cr Cu La Ni Pb Sc V Zn C Org. C I Jy Mn I Co Cr Cu La Ni Pb Sc V Zn C Org. C I Jy Mn I Co Cr Cu La Ni Pb Sc V Zn C Org. C I Jy Mn I Co Cr Cu La Ni Pb Sc V Zn C D Cr Cu C Cr Cu La Ni Pb Sc V Zn C D Cr Cu C Cr Cu La Ni Pb Sc V Zn C D Cr Cu C Cr Cu La Ni Pb Sc V Zn C D Cr Cu C Cr Cu La Ni Pb Sc V Zn C D Cr Cu C Cr Cu La Ni Pb Sc V Zn C D Cr Cu C Cr Cu La Ni Pb Sc V Zn C D Cr Cu C Cr Cu La Ni Pb Sc V Zn C Cr Cu C Cr Cu La Ni Pb Sc V Zn C Cr Cu C Cr Cu C Cr Cu La Ni Pb Sc V Zn C Cr Cu Cu C Cr Cu C Cr Cu C Cr Cu Cu C Cr Cu Cu C Cr Cu C Cr Cu C Cr Cu Cu Cu C Cr Cu Cu Cu Cu C Cr Cu	Station Longitude Latitude	Long	i tude	Lat	itude	Water	Deptinter	th		<u></u>	0	leme	+5	n par	+-	E .	=	+			Pe	rcent	
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^{*} Zero following number indicates grab sample; 2 indicates 2-inch core; 3 indicates 3-inch core. † Zero indicates element not determined; zero preceded by minus sign indicates element was not detected.

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	Zn	385 271 124 73	0	310 303 308 65 65	308 222 158 158 89 72 61	58 233 54 54	427 331 157 59	269 1111 76 80 76	88	71 77 77 62 62
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	m	55 49 49 51	0	40 41 42 38 37	300 6 6 7 3 3 3 3 4 6 6 7 3 5 6 6 7 3 5 6 6 7 3 5 6 6 7 3 5 6 6 7 5 6 6 7 5 6 7	21 23 15 19 17	4 4 4 8 3 3 3 5 6 6 6 6 6 6 6 6 6 6 6 6 6 6 6 6	45 44 57 50	00	64 64 56 76 76 76
	_	2.0	5.0	30°0 94°0	5.0 10.0 15.0 20.0 25.0 40.0	3.0	2.0 4.0 7.0	3.0 6.0 6.0 9.0 0.4 0.3	2.5	3.0 6.0 9.0, 74.0
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Water	(++)	250	86	168	195	102	230	276	312	213
i +ude	(min)	25.89	86 34.09	37.00	39.69	36.50	86 43.79	48.09	1.79	6.50
Lat	(deg	86	86	86	98	8	86	98	87	81
i +ude	(deg)(min)(deg)(min	59.25	42 11.19	13.79	16.69	8.00	60.6	9.79	12.00	2 * 00
Long	(deg)	45	42	45	45	45	45	45	45 1	45
Station Longitude Latitude	no. * (101-3	103-0	105-3	107-2	110-3	113-3	115-3	118-0	122-2

* Zero following number indicates grab sample; 2 indicates 2-inch core; 3 indicates 3-inch core. † Zero indicates element not determined; zero preceded by minus sign indicates element was not detected.

TABLE 1 — Continued

* Zero following number indicates grab sample; 2 indicates 2-inch core; 3 indicates 3-inch core.
† Zero indicates element not determined; zero preceded by minus sign indicates element was not detected.

TABLE 1 — Continued

			Water	Denth	fh fh																
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	0	67077	717	-0-	10.0	37	2.2	27	00	52	23	20	32	49	00	54 1	149	1.62	21	.040	
				10.0-	14.0	35	1.6	18	0	46	13	19	22	18	0	400	41	0.85	23	.040	
				10 01	1 2 0	9.6	1.3	30 ==	0	20	15	22	56	20	0	54	58	1.22	19	040*	
41 50.00 87	8.7	87 23.75	5.1	-0.0	10.2	6	9.0	0-	7	22	1	8	80	28	ተጎ	16	63	0.19	2	.02.	
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				5.1-	15.2	68	1.8	0	17	63	31	27	35	32		9.8	7.1	1.31	41	090	
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* Zero following number indicates grab sample; 2 indicates 2-inch core; 3 indicates 3-inch core. † Zero indicates element not determined; zero preceded by minus sign indicates element was not detected.

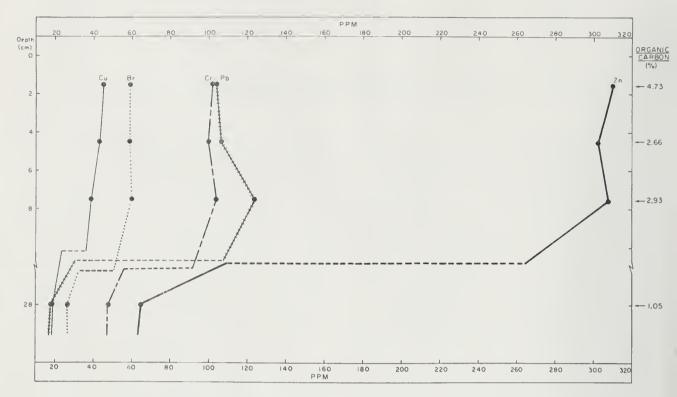


Fig. 2 - Distribution of bromine, chromium, copper, lead, zinc, and organic carbon in Lake Michigan core 105.

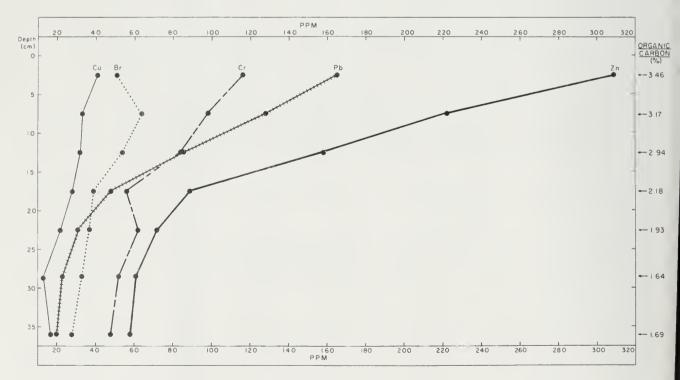


Fig. 3 - Distribution of bromine, chromium, copper, lead, zinc, and organic carbon in Lake Michigan core 107.

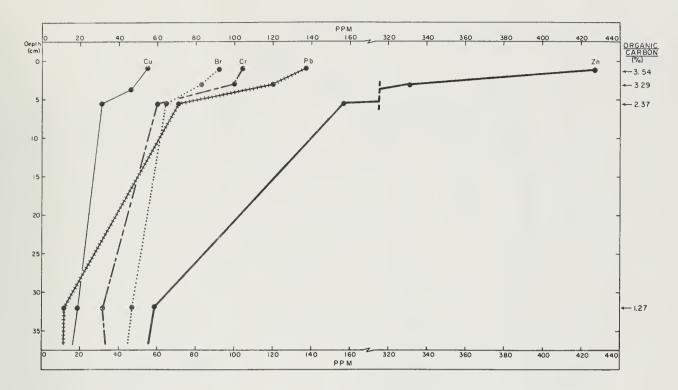


Fig. 4 - Distribution of bromine, chromium, copper, lead, zinc, and organic carbon in Lake Michigan core 113.

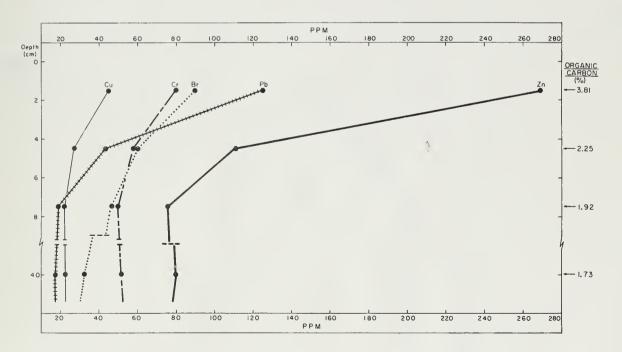


Fig. 5 - Distribution of bromine, chromium, copper, lead, zinc, and organic carbon in Lake Michigan core 115.

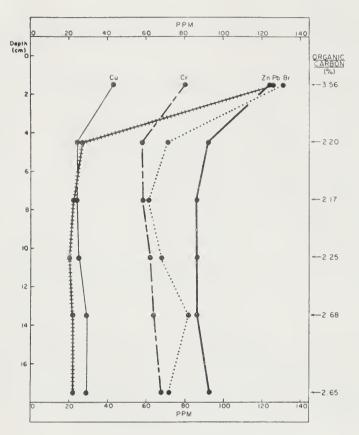
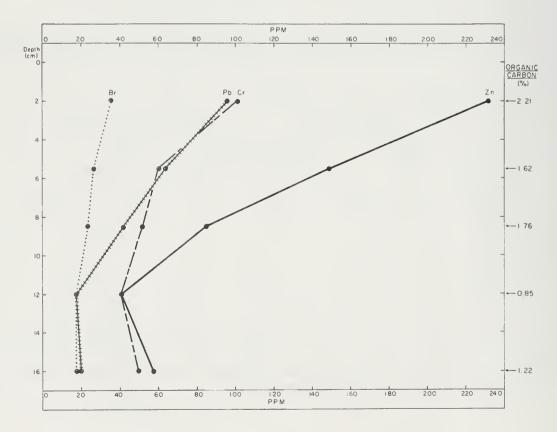


Fig. 6 - Distribution of bromine, chromium, copper, lead, zinc, and organic carbon in Lake Michigan core 124.

Fig. 7 - Distribution of bromine, chromium, lead, zinc, and organic carbon in Lake Michigan core 241.



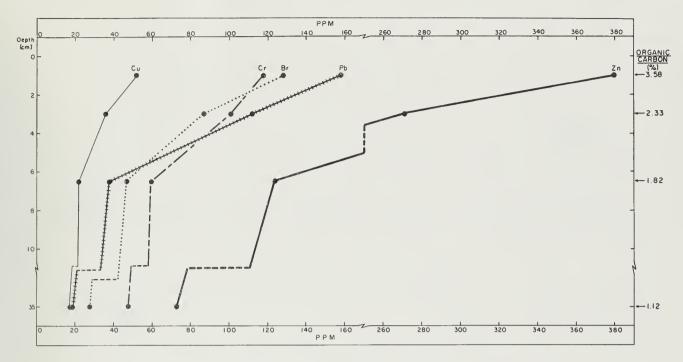


Fig. 8 - Distribution of bromine, chromium, copper, lead, zinc, and organic carbon in Lake Michigan core 101.

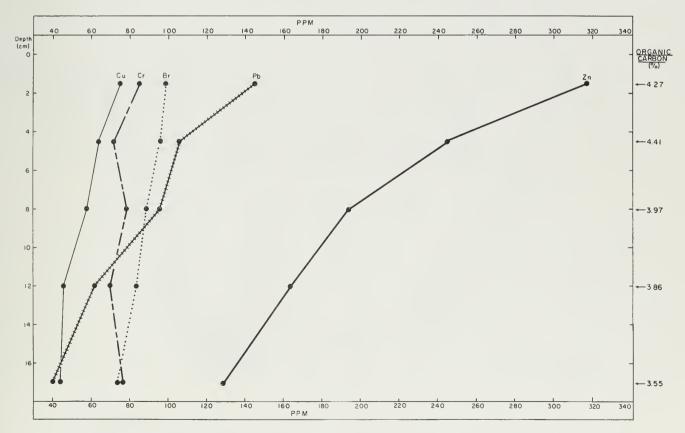


Fig. 9 - Distribution of bromine, chromium, copper, lead, zinc, and organic carbon in Lake Michigan core 150.

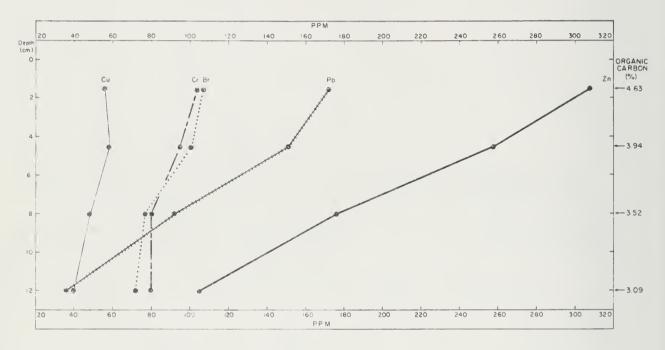


Fig. 10 - Distribution of bromine, chromium, copper, lead, zinc, and organic carbon in Lake Michigan core 51.

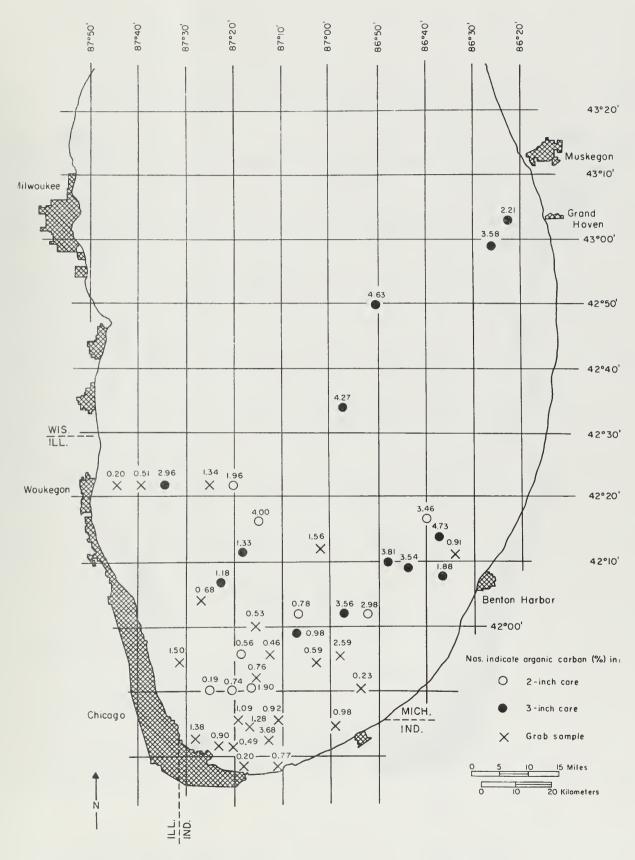


Fig. 11 - Percentage of organic carbon in the most recent sediments of southern Lake Michigan.

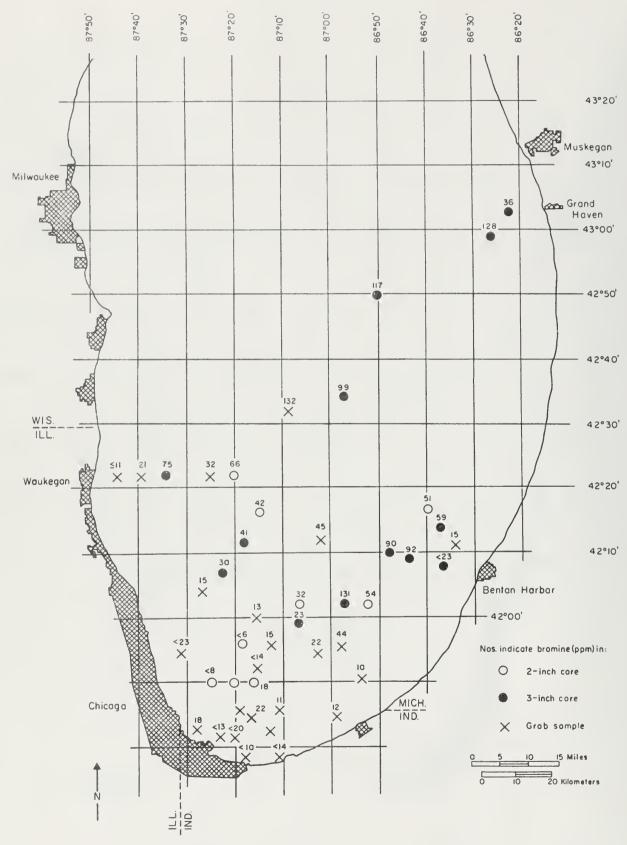


Fig. 12 - Concentration (ppm) of bromine in the most recent sediments of southern Lake Michigan.

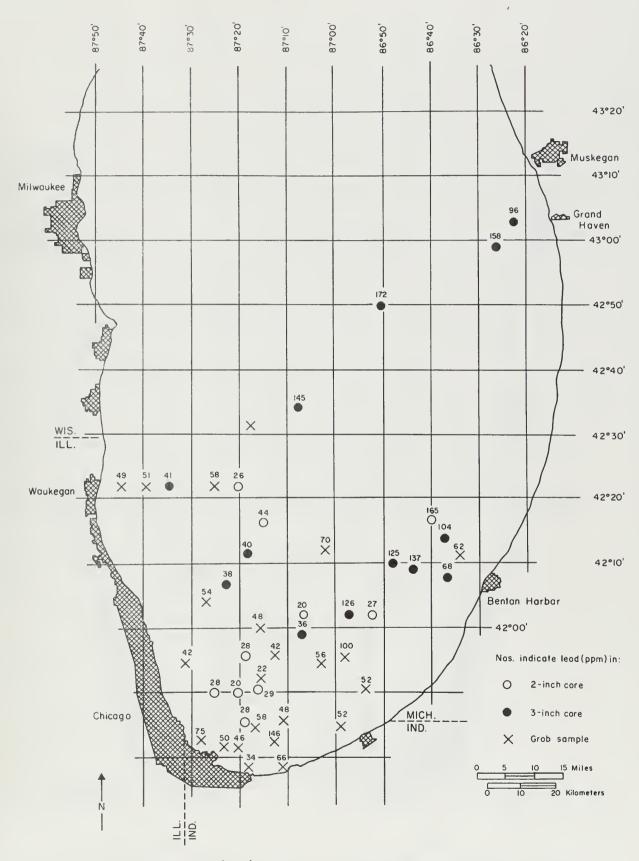


Fig. 13 - Concentration (ppm) of lead in the most recent sediments of southern Lake Michigan.

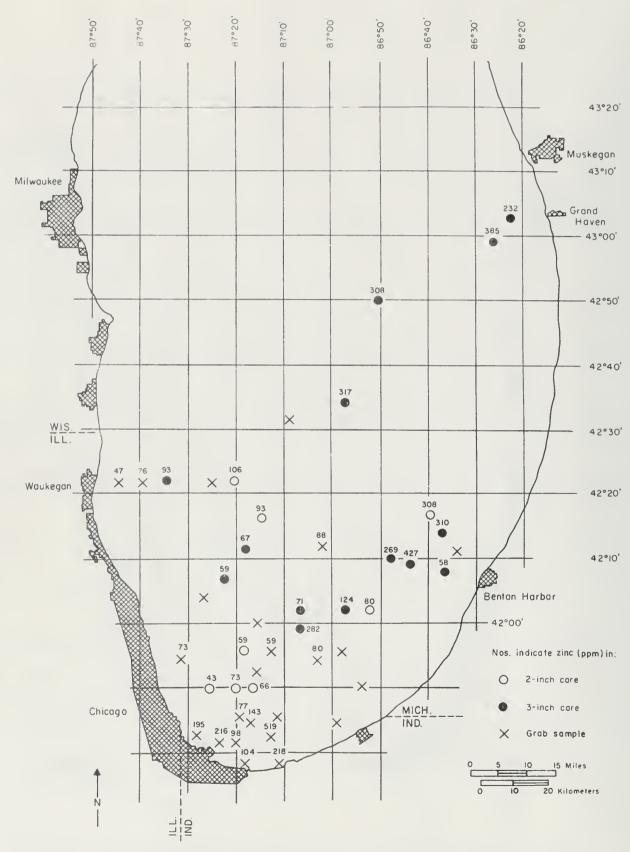


Fig. 14 - Concentration (ppm) of zinc in the most recent sediments of southern Lake Michigan.

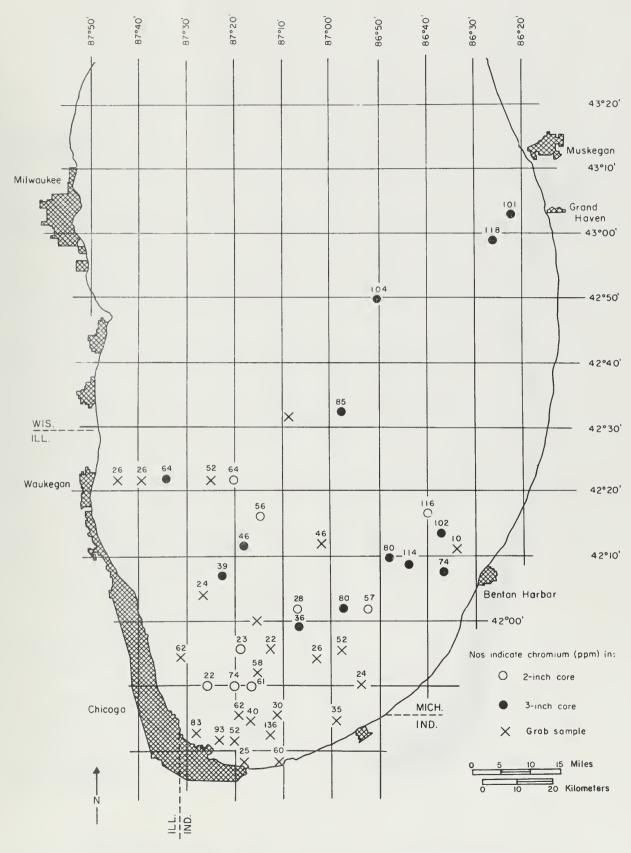


Fig. 15 - Concentration (ppm) of chromium in the most recent sediments of southern Lake Michigan.

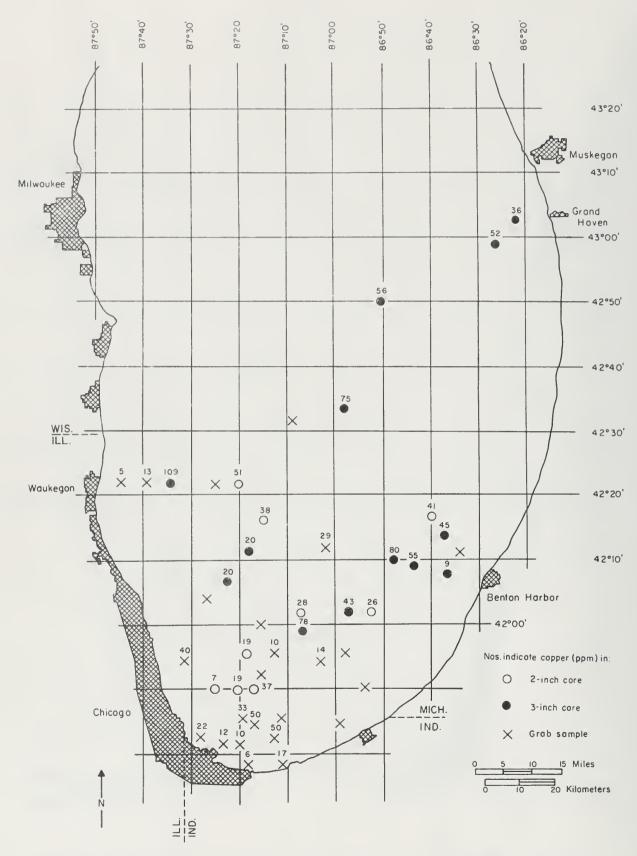


Fig. 16 - Concentration (ppm) of copper in the most recent sediments of southern Lake Michigan.

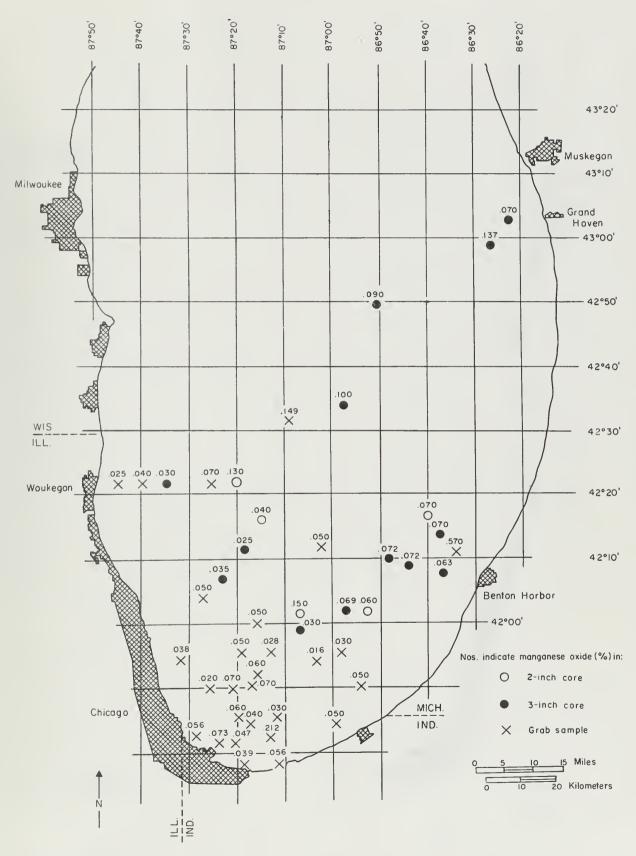


Fig. 17 - Percentage of manganese oxide in the most recent sediments of southern Lake Michigan.

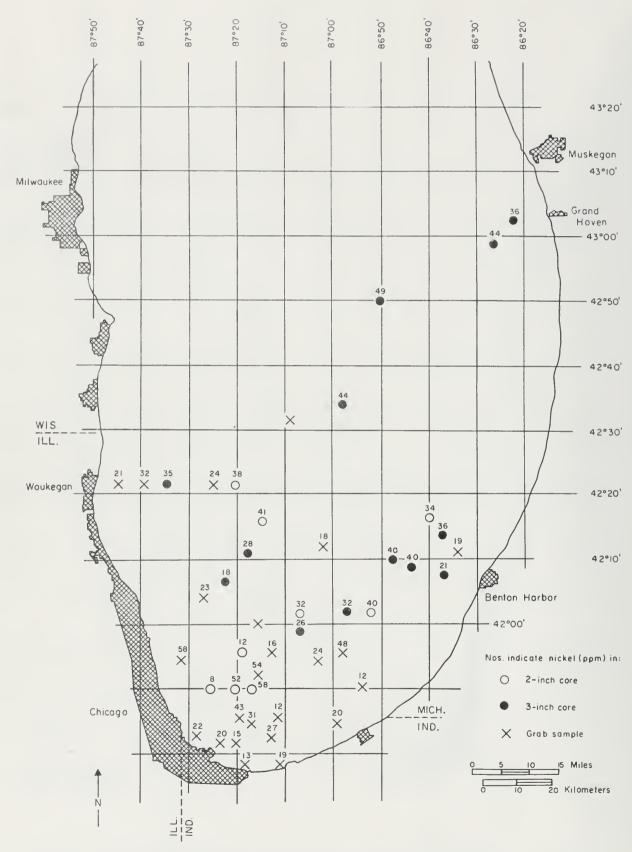


Fig. 18 - Concentration (ppm) of nickel in the most recent sediments of southern Lake Michigan.

TABLE 2-AVERAGE CONCENTRATIONS OF TRACE ELEMENTS, IRON OXIDE, ORGANIC CARBON, AND LESS THAN 2-MICRON CLAY IN SOUTHERN LAKE MICHIGAN CORES

Constituent	Top interval*	*_	1 - 7 c	CM	4 - 12 0	cm	8 - 20 cm	æ	16 cm and dee	deeper
Br (ppm)	65 ± 38	(17)	60 ± 29	(12)	47 ± 21	(18)	η2 ∓ 8 <i>η</i>	(11)	35	(19)
Cr (ppm)	70 ± 30	(22)	66 ± 22	(15)	57 ± 20	(21)	55 ± 16	(16)	52	(54)
Cu (ppm)	41 ± 24	(22)	33 ± 14	(15)	28 ± 10	(21)	27 ± 9	(19)	20 ± 9	(54)
(mdd) qd	79 ± 54	(22)	65 ± 45	(15)	75 ± 44	(21)	30 ± 18	(19)	20 ± 3	(23)
Zn (ppm)	179 ± 125	(22)	148 ± 107	(15)	115 ± 71	(21)	86 ± 38	(19)	66 ± 12	(23)
(mdd) in	34 ± 12	(22)	32 ± 8	(15)	34 ± 8	(21)	33 ± 11	(19)	35 ± 6	(23)
Mn0 (%)	0.065 ± 0.033 (22)	(22)	0.070 ± 0.022	(15)	0.067 ± 0.023	(21)	0.057 ± 0.023	(16)	0.050 ± 0.018	(54)
Fe ₂ 0 ₃ (%)	3.99 ± 1.28	(22)	3.91 ± 1.02	(15)	3.81 ± 1.03	(21)	3.54 ± 1.17	(16)	3.35 ± 0.65	(54)
Organic carbon (%)	2.35 ± 1.44	(22)	2.03 ± 1.20	(15)	1.85 ± 0.95	(21)	1.88 ± 1.04	(19)	1.40 ± 0,48	(23)
< 2µ clay (%)	31.6 ± 19.3 (20)	(20)	29.7 ± 13.6	(14)	34.5 ± 10.8	(19)	34.3 ± 15.6	(18)	41.4 ± 8.8	(54)

* Values given for each interval are, in order, average trace element concentration, standard deviation, and number of samples used to compute the mean.

[†] Numbers enclosed in parentheses equal number of samples used in calculating the correlation coefficient.

IN ALL CORE SECTIONS WITH ORGANIC CARBON, < 2μ CLAY, WATER DEPTH, Fe $_20_3$, AND MnO TABLE 3-CORRELATION OF SELECTED TRACE ELEMENTS

					7					
Sediment	Br	Cr	Cu	Pb	Zn	ž	MnO	Fe ₂ 0 ₃	Organic	< 2µ clay
Top Organic carbon < 2µ clay Water depth	0.77 (17)* 0.58 (15) 0.62 (17) 0.44 (17)	0.80 (22) 0.50 (20) 0.44 (22) 0.78 (22)	0.49 (22) 0.04 (20) 0.51 (22) 0.28 (22)	0.86 (22) 0.26 (20) 0.66 (22) 0.61 (22)	0.73 (22) 0.21 (20) 0.58 (22) 0.54 (22)	0.48 (22) 0.70 (20) 0.30 (22) 0.69 (22)	0.37 (22) 0.84 (20) 0.37 (22) 0.76 (22)	0.65 (22) 0.63 (20) 0.37 (22)	0.34 (20) 0.70 (22) 0.65 (22)	0.34 (20)
Mno	0.40 (17)	_		00 00	36 (.48 (2	,	0.76 (22)		.64 (2
<u> </u>				(,				,
Organic carbon < 2µ clay		_		40	82 (1 39 (1	.76	0.46 (15)	(15)		0.39 (14)
Water depth Fe ₂ 0 ₃				0.43 (15)	0.40 (15)	0.73 (15)			0.74 (15)	0.23 (14)
MnO	0.41 (12)	0.47 (15)	0.44 (15)	0	40 (1	.45		0.71 (15)		39
4 - 12 cm										
Organic carbon < 2µ clay	0.93 (18) 0.73 (17)	0.87 (21)	0.77 (21)	0.76 (21)	0.66 (21)	0.57 (21)	0.27 (21)	\sim		0.63 (19)
Water depth	0.61 (18)	0.29 (21)	0.73 (21)	9 0	23	0.68 (21)		0.52 (21)	0.64 (21)	0.50 (21)
MnO				10	547	_	-	0.61 (21)	27 (.35 (
8 - 20 cm										
Organic carbon	0.92 (17)	0.94 (19)	0.85 (19)	0.61 (19)	68 (1)	88 0	0.59 (19)	0.83 (19)	C	0.90 (18)
Water depth				34 (1	59 (1	81 (1	0.74 (19)	89 (1	3 (7	.86 (1
Fe203 Mn0	0.61 (17)	0.79 (19)	0.76 (19)	0.54 (19)	0.58 (19)	0.80 (19)	1	0.77 (19)	0.83 (19)	0.83 (19)

* Numbers enclosed in parentheses equal number of samples used in calculating the correlation coefficient.

organic carbon concentration also is shown. These sediments, located off the mouth of the Grand River at Grand Haven, have accumulation and distribution patterns similar to those of the sediments off Benton Harbor, Michigan.

Distributions of the same constituents in cores 150 and 51, which were collected near the center of the southern basin of Lake Michigan, are shown in figures 9 and 10. High concentrations of lead, zinc, and organic carbon in the top 6 to 8 centimeters of sediment are evident; bromine, copper, and chromium have accumulated to a lesser degree near the sediment-water interface. In a previous publication, Shimp, Leland, and White (1970) showed that Lake Michigan sediments off Waukegan, Illinois, also exhibit trace element concentrations in the first few centimeters of sediment.

The concentrations of organic carbon, bromine, lead, zinc, chromium, copper, manganese oxide, and nickel in the top, or first, sediment intervals for all samples are shown in figures 11 through 18. The higher concentrations of bromine (fig. 12), lead (fig. 13), zinc (fig. 14), chromium (fig. 15), and copper (fig. 16) occur in the sediments containing the highest amounts of organic carbon (fig. 11), which, in general, are located off Benton Harbor and Grand Haven, Michigan, off Waukegan, Illinois, and in the center of the southern lake basin. Manganese oxide (fig. 17) is similarly distributed, except that variations in concentration are not as large as those for the other trace elements, and high concentrations are absent in sediments off Benton Harbor. Nickel concentrations (fig. 18) exhibit no consistent trend.

Average concentrations of trace elements, iron oxide, organic carbon, and less than 2-micron clay are given in table 2 for five sediment depth intervals in all cores. Although the sediment intervals overlap, results from any single interval have been averaged only once, that is, a 0 to 4 cm top interval is not included in a 1 to 7 cm interval. Iron oxide is included in table 2 because of its possible influence on the distribution of manganese and other trace elements. Complete determinations of iron and other major elements found in Lake Michigan sediments will be reported in a forthcoming Environmental Geology Note. Average concentrations of bromine, chromium, copper, lead, zinc, and organic carbon decrease noticeably with increasing sediment depth (table 2), iron oxide concentrations decrease slightly, and nickel, manganese oxide, and less than 2-micron clay values show no definite trend. These results agree well with trace element concentrations shown in figures 11 through 18.

Correlation data for those trace elements that exhibit at least an occasional tendency to accumulate in sediments near the sediment-water interface are summarized in table 3. Correlation coefficients, calculated from all cores, are given for each trace element versus organic carbon, less than 2-micron clay, water depth, iron oxide, and manganese oxide at four sediment depth intervals. Observations based on the data in table 3 include:

Bromine—good correlations with organic carbon throughout all sediment intervals; at depths greater than 4 cm, correlations with less than 2-micron clay improve.

- Chromium—best correlations with organic carbon throughout all sediment intervals; good correlations with iron oxide.
- Copper—good correlations with organic carbon throughout all sediment intervals; correlations with clay, iron oxide, and manganese oxide improve with depth.
- Lead—good correlations with organic carbon throughout all sediment intervals.
- Zinc—good correlations with organic carbon throughout all sediment intervals.
- Nickel—somewhat better correlations with iron oxide and, possibly, clay than with the other constituents.
- Manganese oxide—good correlations with iron oxide throughout all sediment intervals.
- Organic carbon—fair correlations with iron oxide; poor correlations with less than 2-micron clay.

DISCUSSION

Little is known about the mechanisms whereby the chemical constituents described here have been incorporated into southern Lake Michigan sediments. Natural phenomena and the activities of man both undoubtedly contribute to the observed accumulation of both organic carbon and trace elements in the surficial sediments. Thus far, the method used to distinguish the quantity of a constituent that is "natural" from that which is a product of civilization has been the comparison of trace element concentrations obtained from newly deposited sediments with those of deeper lying, older sediments. The older deposits most nearly reflect the natural or pre-civilization trace element composition of the sediments.

It is clear that substantial quantities of elements that are toxic to aquatic life at very low concentrations in water do enter southern Lake Michigan in surface drainage from the surrounding watershed and from the atmosphere. Many of these elements, including those described in this report, become part of the suspended particulate matter, which is subsequently transported by current action and deposited in quiet regions of the lake. Considering the results of this study and the history of waste discharges to southern Lake Michigan, it is logical to proceed on the theory that a significant portion of the observed accumulations is the result of pollution. Because organic carbon is closely correlated with trace element concentration, it is also reasonable to assume that soluble or colloidal organometallic complexes play an important role in the transport and sedimentation of trace elements in southern Lake Michigan, for such complexes are readily adsorbed by suspended clays and precipitates.

SUMMARY

Bromine, chromium, copper, lead, and zinc are concentrated in the uppermost, or recently deposited, portions of organic-rich, fine-grained, southern Lake Michigan sediments. High concentrations of these elements correlate more closely with the amounts of organic carbon present than with clay-size material, water depth, iron oxide, or manganese oxide. Off major river mouths, trace elements have accumulated to greater depths within the sediments in deeper regions of the lake, which is probably a result of high depositional rates associated with the rivers' large sediment load. Similar accumulation patterns for arsenic and total phosphorus concentrations in southern Lake Michigan sediments have been reported by Ruch, Kennedy, and Shimp (1970), and Schleicher and Kuhn (1970).

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